

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Report 7980	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PERSONAL ATMOSPHERIC GAS SAMPLER WITH A CRITICAL ORIFICE, PART 2—SYSTEM FOR HANDLING AND ANALYZING THE GAS FROM THE SAMPLER		5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL Problem
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) H. G. Eaton, J. P. Stone, and F. W. Williams		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, D.C. 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NRL Problem C08-40 Project NIOSH-IA-74-9
11. CONTROLLING OFFICE NAME AND ADDRESS National Institute for Occupational Safety and Health Rockville, Md. 20882		12. REPORT DATE March 22, 1976
		13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Air pollution Time-integrated air sampler Personal gas sampler Industrial atmospheres		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  A gas handling and analyzing system has been developed to analyze, in the range of 1 ppm, unwanted atmospheric contaminants collected and stored at subambient pressures in a suitable container such as the personal gas sampler developed by NRL for the National Institute for Occupational Safety and Health. One of two subsystems detects individual organic contaminants or, by using a backflush valve, detects the concentration of total hydrocarbons by regrouping  (Continued)		

the components into one measurable peak. The backflush valve is used also to clean the column after the analysis of individual components prior to subsequent analysis. The other subsystem detects methane and carbon monoxide.

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## PERSONAL ATMOSPHERIC GAS SAMPLER WITH A CRITICAL ORIFICE

### PART 2 — SYSTEM FOR HANDLING AND ANALYZING THE GAS FROM THE SAMPLER

#### INTRODUCTION

In accordance with a memorandum of agreement between the Naval Research Laboratory, and the National Institute for Occupational Safety and Health (No. NIOSH-IA-74-9) the following report is presented as a supplement to NRL Report 7963, "Personal Atmospheric Gas Sampler with a Critical Orifice, Part 1—Development and Evaluation," by H. G. Eaton, J. P. Stone, and F. W. Williams dated February 13, 1976.

Although the analysis of various atmospheric contaminants has become fairly routine in recent years, special considerations must be given to handling and analyzing contaminants collected and held at subambient pressures in containers such as the NRL personal atmospheric gas sampler. The following main text is a detailed description of the gas-handling system and analysis scheme employed to extract the contaminants from the personal sampler and its analysis.

Appendix A is a discussion of the method in conjunction with alternate methods and columns that were used or were considered for gas handling and analysis.

#### GENERAL DESCRIPTION OF THE SYSTEM

A Beckman GC-5 gas chromatograph equipped with a thermal conductivity cell and dual hydrogen-flame ionization detectors was used to evaluate the performance of the personal sampler. This analyzer was modified considerably to prepare the subambient pressured sample for analysis and achieve the desired separation and detection of the contaminants of interest.

A schematic of the gas handling-analytical system is shown in Fig. 1. Subsystem I was designed to detect the organic atmospheric contaminants including ethane, Freon-12, vinyl chloride, Freon-11, vinylidene chloride, hexane, benzene, and "total hydrocarbons." The analysis of "total hydrocarbons" is discussed in Appendix A. Subsystem II was designed to detect methane and carbon monoxide.

The gas sampling and backflush valves were manufactured by Carle Instruments, Incorporated, Fullerton, California. Other valves used were stainless-steel ball valves ( $V_1$ ,  $V_5$ ,  $V_6$ ,  $V_7$ ), toggle valves ( $V_2$ ,  $V_3$ ,  $V_4$ ), and fine metering valves ( $V_8$ ,  $V_9$ ). All tubing was of stainless steel. Tubing connections to and from sampling valves, subsystems I and II, were 1.6 mm (1/16 in.) o.d. The sample loops were 6.4 mm (1/4 in.) o.d. and of 8 cm<sup>3</sup> and 40 cm<sup>3</sup> volume for subsystems I and II respectively. The tubing from

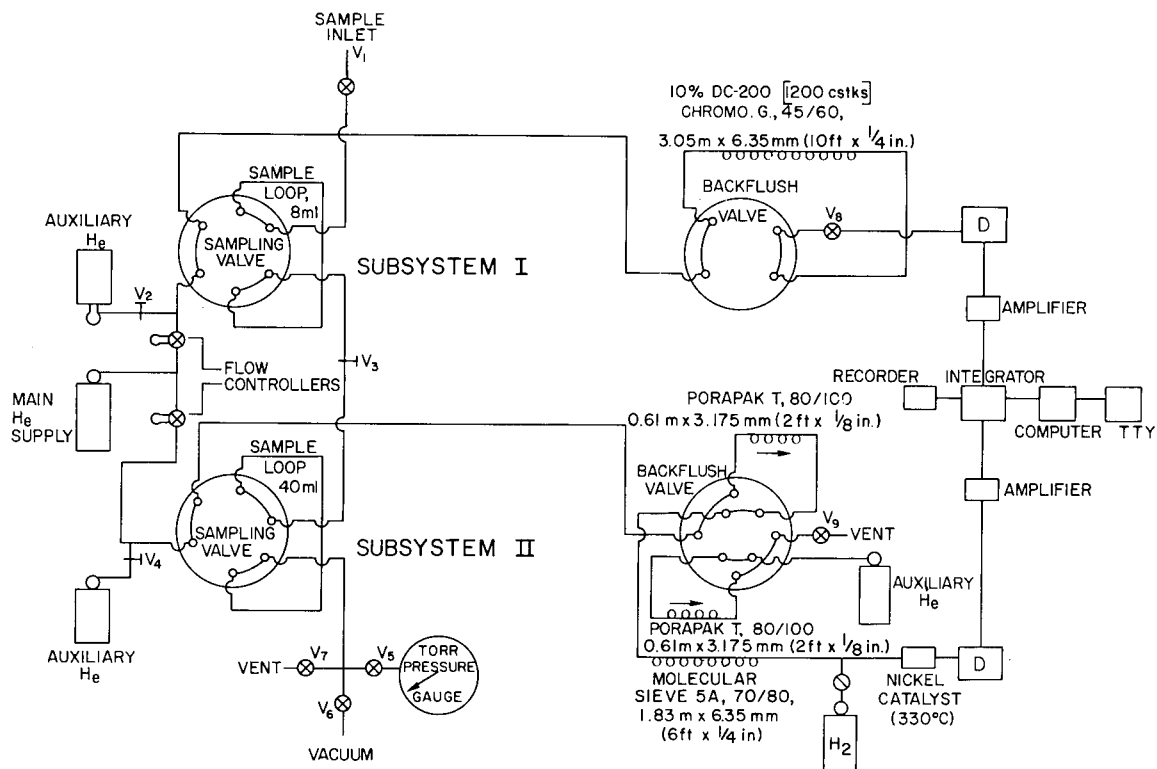


Fig. 1—Gas handling and analyzing system

valves  $V_2$  and  $V_4$  was 3.2 mm (1/8 in.) o.d. To measure the sample pressure accurately, a Wallace and Tiernan, Model 62A-4A-0100D, 0 to 5000 torr, pressure gauge was connected by a cross, via valve  $V_5$ , to the sample line. A vacuum system was connected at valve  $V_6$  leading also to the cross.

Flow controllers in the main helium supply to the sampling valves were standard parts of the Beckman GC-5 gas chromatograph. Secondary or auxiliary helium flows were brought in downstream of the flow controllers through  $V_2$  and  $V_4$  to provide a high-volume flow for rapid compression of the sample during injection [1]. In subsystem I, valve  $V_8$  was used as a restrictor and employed to prevent the flame ionization detector (D) from blowing out when the backflush valve was actuated. The detection of the individual and total hydrocarbons was conducted in accordance with the procedures given by Eaton et al. [2]. In subsystem II the detection of CO with the flame ionization detector was accomplished by converting CO to  $\text{CH}_4$  over a nickel catalyst [3]. To prevent the contamination of the Molecular Sieve columns by the other contaminants in the sample, a backflush valve equipped with two precolumns, both Porapak T, 80/100 mesh, 0.6 m by 3.2 mm, was used. Valve  $V_9$  served as a restrictor to minimize pressure fluctuations when this backflush valve was actuated.

The separation column of subsystem I and its backflush valve, and the separation column of subsystem II, Molecular Sieve, were operated at 85°C. The nickel catalyst was

operated at 330°C, and the detector temperature was 150°C. All other components of the system were operated at room temperature.

The flow rate of the carrier gas through both subsystems I and II was 60 ml/min. To obtain ideal detector performance from the flame ionization detector, an additional 60 ml/min of helium flow (a total flow of 120 ml/min) was passed through the detector (not shown in Fig. 1). Hydrogen flow was 50 ml/min in each system. As shown, H<sub>2</sub> for subsystem II was added to the catalyst, whereas for subsystem I, H<sub>2</sub> was added at the detector.

The response from the flame ionization detector through the amplifier is fed into an integrator (Hewlett-Packard, Model 3370B) and a 1-mV strip chart recorder. The digitized signal is processed by a Hewlett-Packard minicomputer, Model 2116C.

## SYSTEM PROCEDURE

### Preparation of the Sampler for Analysis

The sampler is prepared for evaluation of its contents by connecting the off-on valve to the gas handling system at the inlet port. With the sampler closed, valves V<sub>1</sub>, V<sub>3</sub>, V<sub>5</sub>, and V<sub>6</sub> are opened to evacuate the sampling system to less than 1 torr pressure. Valve V<sub>6</sub> is then closed. By opening the off-on valve of the sampler, valve V<sub>1</sub> is used to meter in the sample to a pressure of 100 torr to both subsystem I and II. Valve V<sub>1</sub> is then closed.

The normal operating or sample pressure of subsystem I is 100 torr and that of subsystem II is 50 torr. To obtain this difference, valve V<sub>3</sub>, which is used to separate the systems, is closed, and the pressure in subsystem II is reduced to 50 torr. Valve V<sub>5</sub> is then closed to avoid damage to the pressure gauge due to sudden pressure surges during the analysis cycle when the injection valves are actuated. Valve V<sub>7</sub> is normally closed and is opened only to vent the positive pressure obtained when the injection valves are reset after the sample has been injected onto the separation columns.

### Subsystem-I Analysis

With the sample contained in the sample loop at a pressure of 100 torr, the sampling valve is rotated to place the loop in the carrier flow. At the same time, valve V<sub>2</sub> is opened to rapidly compress the sample and force it into the smaller diameter tubing leading to the backflush valve and column. After 20 seconds the sampling valve is returned to its original position and valve V<sub>2</sub> is closed. The flow controller now controls the flow of the carrier gas. After the detection of the individual contaminants of interest, the backflush valve is actuated to reverse the flow of the carrier through the column and thereby regroup the less volatile components of the injected sample into one measurable peak. In the experimental work n-decane was used to represent these less volatile compounds.

The results of a sample collected and analyzed from the personal sampler are shown in Fig. 2. At the completion of approximately 12 minutes, the backflush valve is actuated.

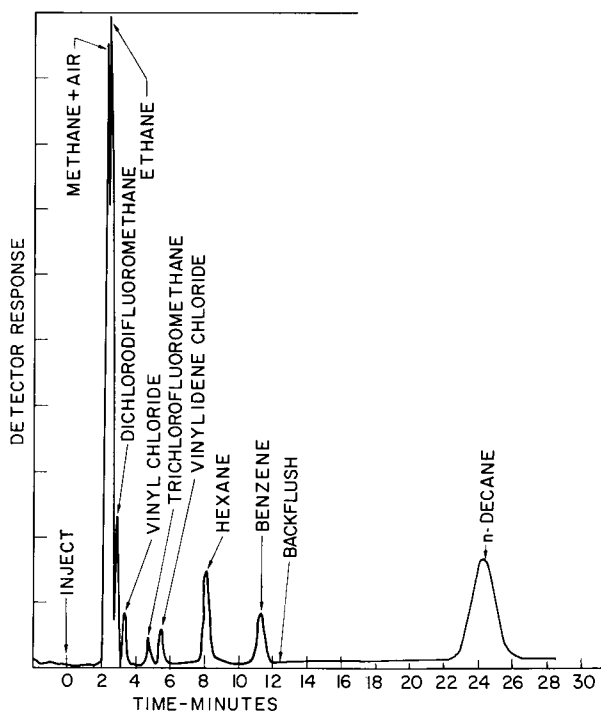


Fig. 2—An analysis of organic contaminants collected from the personal atmospheric gas sampler

The backflush peak (n-decane) is detected in approximately the same time as the foreflush elapsed time. The retention times of several other possible contaminants are listed in Table 1.

### Subsystem-II Analysis

Subsystem II was designed to detect  $\text{CH}_4$  and  $\text{CO}$ . Although the detection of these components is fairly routine and is accomplished on a Molecular Sieve column, caution must be exercised so that this column does not become contaminated with the other components of the sample. To avoid this contamination, two precolumns, Porapak T, 80/100 mesh, 0.6 m by 3.2 mm, operated at room temperature are used to separate  $\text{CH}_4$  and  $\text{CO}$  from the other gases in the injected sample. This separation is done by backflushing the other gases still on the precolumn after the  $\text{CH}_4$  and  $\text{CO}$  have passed through.

The sequence of operation (Fig. 1) is as follows: With the sample enclosed in the sample loop at a pressure of 50 torr, the sampling valve is rotated to place the loop in the carrier gas stream. At the same time, valve  $V_4$  is actuated for 35 seconds to rapidly inject the sample as described for subsystem I. At the end of this time the injection valve is returned to its original start position and valve  $V_4$  is closed. At 55 seconds the  $\text{CH}_4$  and  $\text{CO}$  have passed through the top precolumn and are on the Molecular Sieve column. The backflush valve is then actuated, turned clockwise, thereby allowing the auxiliary carrier to flow in the opposite direction on the top column carrying the contaminants out



Table 1—Retention Times of Other Contaminants of Interest on a DC-200 Separation Column

Component	Retention Time (min)
Methane plus air	2.30
Ethane	2.50
Dichlorodifluoromethane plus n-propane	2.92
1,2-Dichlorotetrafluoroethane	3.22
Vinyl chloride	3.44
Butane	3.62
Trichlorofluoromethane	4.90
Pentane	5.15
Vinylidene chloride	5.57
1,1,2-Trichlorotrifluoroethane	5.90
Hexane	8.40
Methyl chloroform	10.65
Benzene	11.67
Trichloroethene	14.21
Heptane	14.42
Toluene	21.14
Octane	26.65
Ethyl benzene	38.09
m-Xylene	39.87
o-Xylene	46.35

through valve  $V_9$ . The main carrier flow continues on the bottom precolumn, now in the opposite direction, to the Molecular Sieve column. The reversal of flow on the precolumns does not affect the normal forward flow of the Molecular Sieve column.

To detect the response of CO with a flame ionization detector, as stated previously, a nickel catalyst is used to convert CO to  $\text{CH}_4$ . Figure 3 illustrates the results obtained.

At the conclusion of this analysis cycle, valves  $V_7$  and  $V_3$  are opened to vent the positive pressure. Valve  $V_7$  is then closed. Valves  $V_5$  and  $V_6$  are opened to prepare both subsystems I and II for the next analysis.

## SUMMARY

A system has been developed to extract and analyze the atmospheric contaminants from the personal atmospheric gas sampler. The analyzer is composed of two subsystems. One subsystem is designed to detect the organic contaminants. This subsystem uses a backflush valve, which adds another dimension in the detection of these contaminants; by backflushing, an investigator is able to detect the less volatile components in the sample as one measurable peak. This procedure serves an additional purpose of cleaning the column and thus precluding the possibility of interferences from the less volatile

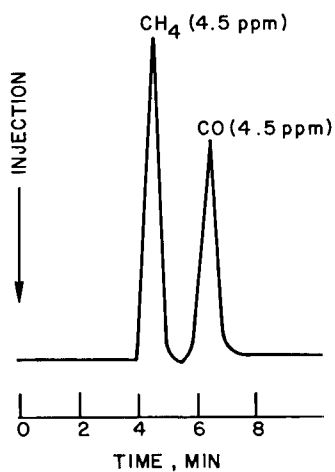


Fig. 3—Analysis of methane and carbon monoxide

components during subsequent analyses. Subsystem II is designed for the detection of methane and carbon monoxide. The procedure and method of analysis delineated affords sensitivity for all components analyzed in the range of 1 ppm.

## APPENDIX A

### ALTERNATE METHODS AND COLUMNS USED FOR ANALYSIS

The following discussion is concerned with various alternate methods of separating the atmospheric contaminants of interest (for subsystem I analysis), a combination injection and backflush valve (also for subsystem I analysis), and a gas handling system for the gas chromatograph which were investigated during the course of this study. Each separation column studied was limited in certain areas and is briefly discussed.

#### COLUMN DEVELOPMENT

##### Method One

By using a Porapak Q column and programming the column temperature from  $-110^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , several contaminants, including CO (Fig. A1), were separated. In this case both a thermal conductivity detector and flame ionization detectors were used in tandem. The advantage of this method is that a one-column system could be used to detect some of the contaminants of interest. The disadvantages of this method are the need of a gas

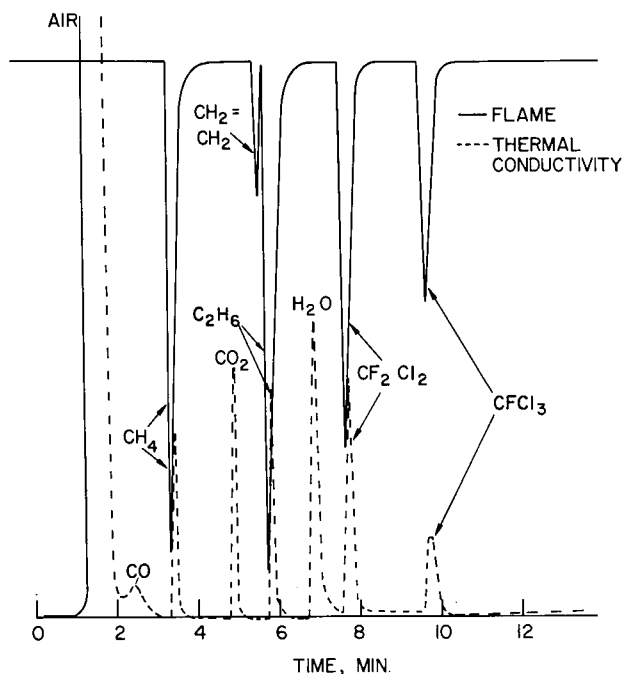


Fig. A1—Analysis of contaminants on a Porapak Q column using programmed temperature:  $-110^{\circ}\text{C}$  to  $150^{\circ}\text{C}$

chromatograph with cryogenic capabilities and the need to accurately program the temperature over a wide range. Further, the retention times for the less volatile contaminants such as benzene are exceedingly long on this type of column as compared to a liquid-phase-partitioning type of column.

## Method Two

In a second method a different porous polymer bead column, Porapak S, was used. In addition a nickel catalyst, with the hydrogen gas leading into it, was placed prior to the detector, as in subsystem II (Fig. 1). This allowed the detection of CO and CO<sub>2</sub> with the flame ionization detector by converting these components into CH<sub>4</sub> [4]. By programming the temperature from 90°C to 140°C, the chromatogram of Fig. A2 was obtained.

The disadvantage of this method is that the response of CO, CO<sub>2</sub>, and Freon-11 decreased after about 2 months, probably due to Freon-11 reacting with and subsequently poisoning the nickel catalyst, thereby affecting the response to both CO and CO<sub>2</sub>.

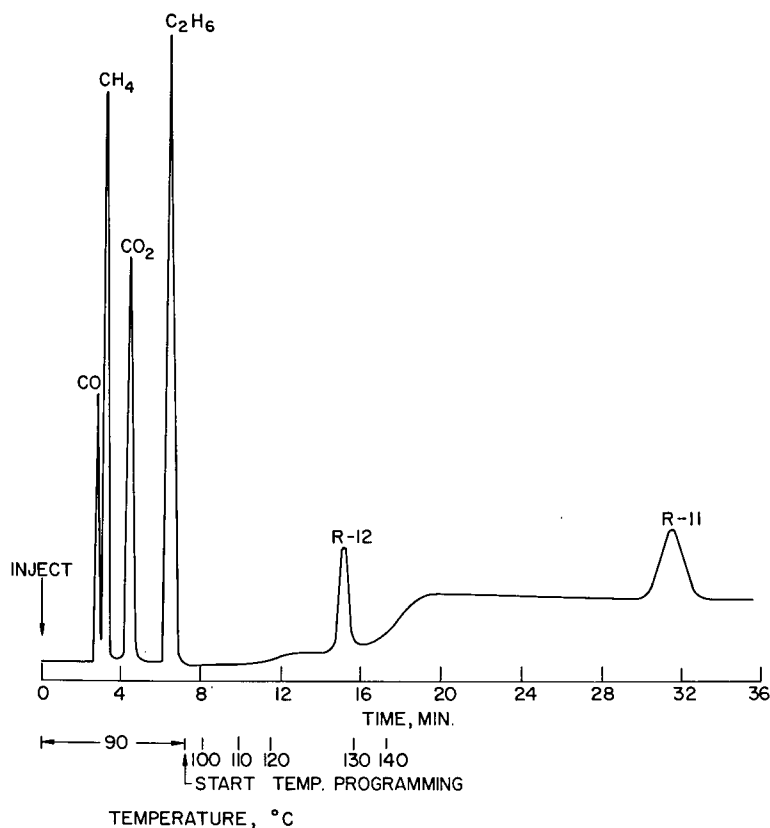


Fig. A2—Analysis of contaminants on a Porapak S column using programmed temperature: 90°C to 140°C

Poisoning of the nickel catalyst would preclude its use for the detection of CO and CO<sub>2</sub> in the flame ionization detector in the presence of chlorocarbons.

### Method Three

The third method represents the present configuration used in subsystem I, in which a partition column, 3 m by 6.4 mm, containing 10% DC-200 on Chromosorb G, 45/60 mesh, was used with the backflush valve shown in Fig. 1. This arrangement allowed for the detection of individual contaminants as well as the detection of "total hydrocarbon" concentrations, which will be defined in the following paragraph. This scheme was initially developed by this Laboratory in response to the Navy's need to know not only the identity of the individual contaminants present in a nuclear submarine atmosphere but also the total hydrocarbon concentration [2].

The atmosphere in a nuclear submarine is a unique environment. The preponderance of the contaminants in the atmosphere are the more volatile compounds: methane and the refrigerants. Thus in the analysis of "total hydrocarbons" the normally high concentrations of the more volatile contaminants are allowed to elute first from the separation column and then the backflush valve is actuated. By this process the carrier gas flow is reversed in the column, and the less volatile components still on the column are allowed to regroup into one measurable peak. This concept is illustrated in Fig. A3, without identifying the individual peaks or contaminants from a submarine atmosphere. The more volatile individual components are eluted up to time 3 minutes, when the backflush valve is actuated to elute the total hydrocarbon peak. The area of this peak is compared with that obtained from a standard containing a known amount of n-hexane. The concentration of "total hydrocarbons" is expressed in milligrams per cubic meter (mg/m<sup>3</sup>) as n-hexane equivalents because of the heterogeneous composition of the mixture.

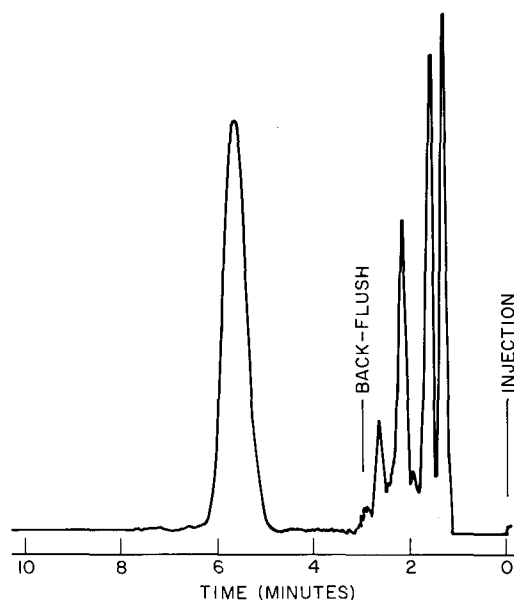


Fig. A3—Analysis and detection of the total hydrocarbon concentration using backflush chromatography of a submarine air sample

It has been found that the width of the backflushed total-hydrocarbon peak is a function of the volatilities of the compounds present [2]. As shown in Fig. A4, a plot of the logarithm of peak width versus carbon number for a series of normal hydrocarbons produced a straight line. Thus it is possible to gain some information from the width of the peak as to the volatility of contaminants present. The dependence of peak width, and thus also peak height, on the volatility of substances backflushed precludes the use of peak height as a quantitative measure of the contaminants present. The area of the peak must be measured.

The detection of additional individual components, those that comprise the bulk of the total peak, is made in a separate run (Fig. A5). In this case the backflush valve is not actuated until 55 minutes. As can be seen at approximately 53 minutes after backflushing, some contaminants still remain on the separation column. Backflushing the column at this time cleans it out prior to subsequent analysis.

As before, the total hydrocarbon concentration is defined as the response obtained from backflushing the separation column after the elution of the normally high concentration of  $\text{CH}_4$  and the refrigerant gases. A similar approach can be used in the analysis

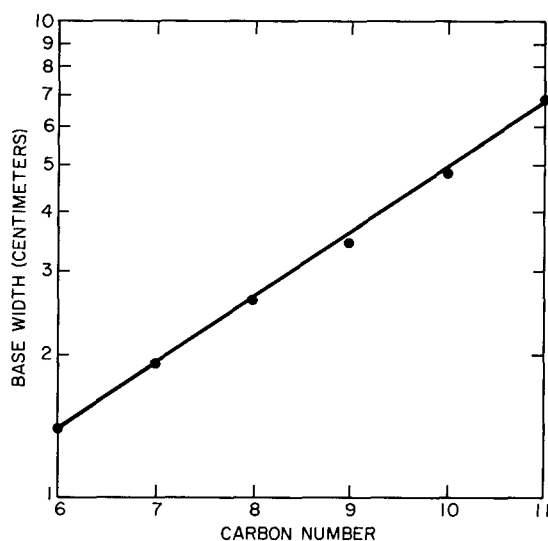


Fig. A4—Effect of sample volatility on the width of the backflush peak

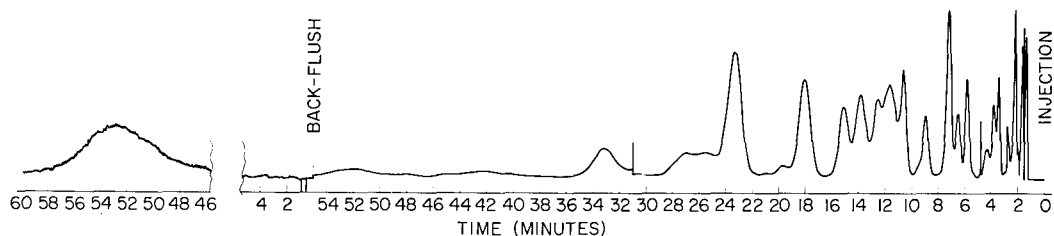


Fig. A5—Delayed-backflush chromatogram of a sample of submarine air

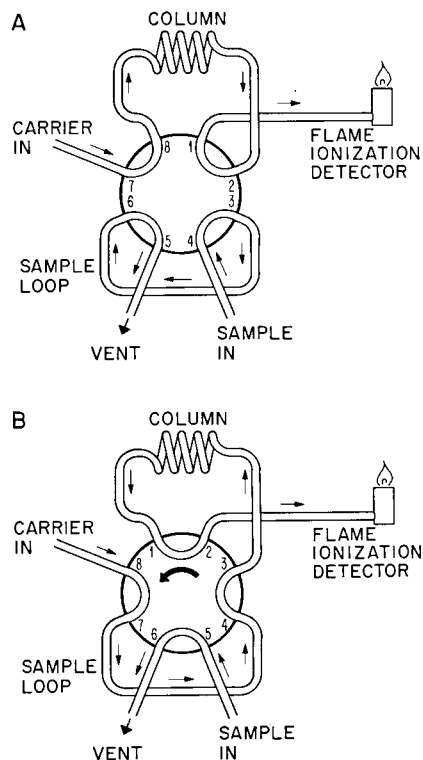
of the contaminants collected with the personal whole-gas sampler. However, if the environment being studied does not contain a normally high concentration of contaminants, then the backflush valve can be actuated any time after the response of the air-plus-methane peak to obtain the total hydrocarbon concentration present.

The advantage of this method is that an investigator can detect not only the individual contaminants present in the atmosphere but the total hydrocarbon concentration as well. The only disadvantage in this scheme is that  $\text{CO}_2$  cannot be detected.

## COMBINATION INJECTION AND BACKFLUSH VALVE

Instead of using the backflush valve shown in Fig. 1, the backflush capability of subsystem I may be accomplished with one valve for injecting and backflushing the sample. As shown in Fig. A6, a single eight-port valve may be used. In position A the carrier gas is directed through the forward end of the column to the flame ionization detector. Meanwhile the sample loop is in position to receive an atmosphere sample. When the valve is rotated to position B, the carrier gas is directed through the sample loop, to the reverse side of the column, and then to the flame ionization detector. After elution of the volatile contaminants, the valve is rotated to position A, and the contaminants remaining in the column are backflushed through the detector.

Fig. A6—Flow diagram of a combination sample-injection and backflush valve. In position A the carrier gas flows through the column to the detector. In position B the carrier gas flows through the sample loop and then in reverse through the column to the detector. In position A the column is being backflushed while the sample loop is receiving an atmospheric sample.



## GAS HANDLING SYSTEM

A schematic of a small vacuum-pressure measuring system is presented in Fig. A7. This system is designed for: measuring the pressure of the sample prior to metering the contents into the gas chromatographic (GC) sample loops, transferring the contents to the sample loops, and evacuating the sampler after analysis is completed. The tubing is 3.2-mm-o.d. 303-type stainless steel. The stainless steel (316) valves are ball type manufactured by Hoke, Inc. (Cresskill, N.J.), the pressure transducer is from Validyne Corp. (Northridge, Calif.) rated at 0 to 1600 torr, the digital panel meter is from Analogic (Wakefield, Mass.), and the 12-volt power supply is from Lafayette (Syosset, N.Y.). The vacuum pump used is a small direct-drive Vac Torr 20 pump (GSA/Precision Scientific Corp., Chicago, Ill.).

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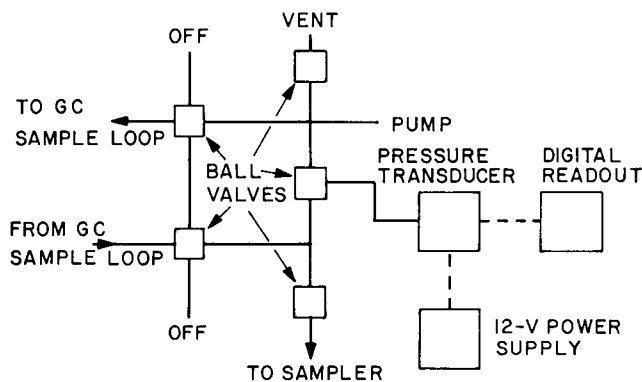


Fig. A7—Small gas handling system